

Graft Copolymerization of Acrylic Monomers onto Coir Dust by Using Gamma Irradiator of Co-60 Source for Superabsorbent Polymer

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Abstract—The graft copolymerization of coir dust and sodium acrylate has been carried out by radiation grafting techniques using gamma irradiator of Co-60. The different parameters such as effect of radiation dose and monomer concentration to the forming gel yield have been studied. Results show the gel content achieved the highest value of 95% at 20 kGy irradiation dose, monomer concentration (50%) and sodium hydroxide concentration (20%). The parameters affect to the swelling behaviour of researched products have been investigated. It is indicated that grafting efficiency increased with the radiation dose but swelling degree decreased with higher irradiation dose. The characteristics of product structure have been determined by SEM and FTIR. The additional peaks observed in FTIR spectra of grafted samples confirmed the grafting of monomer onto coir dust and SEM image showed the morphological changes after grafting of acrylic acid onto coir dust.

Keywords—Gamma Irradiation, Coir Dust, Acrylic Acid, Potassium Hydroxide, Graft Copolymerization, Characterization.

I. INTRODUCTION

Superabsorbent polymer (SAP) is one of the materials which can absorb water from hundreds or thousands of times compare with their original weight [1]. SAP is a polymer only swell but insoluble in water. Superabsorbent polymers are a class of hydro-gel like materials with increasing interest in agriculture or in polluted lands. These hydrogels can be applied in a wide range of products and areas (e.g., hygiene, biomedical, pharmaceutical, agriculture) due to their unique properties such as hydrophilicity, biocompatibility and especially high absorption capacity and swelling/de-swelling behaviour. Practically, SAPs appear as materials with promising characteristics to improve the use of water in soils. These materials can maximize water availability and increase crop production without adverse consequences for the natural resources and environment [2].

Currently, most of the super-absorbents used in practice is mainly petroleum-based synthetic polymers with high production cost and poor environmentally friendly characteristics, and thus the study and development of natural polymer-based super-absorbents has become subject of great interest due to their commercial and environmental advantages

[7]. Therefore, many natural polysaccharides such as starch, cellulose and alginate etc. and their derivatives have been adopted to prepare new type of super-absorbents [6]. Coco peat, also known as coir pith, coir dust is obtained from husk of the coconut, which are by products of other industries that use coconuts. Coir dust is strongly absorbs liquids and gases [7]. This property is due in part to the honeycomb like structure of the mesocarp tissue which gives it a high surface area per unit volume. Coir dust is also hydrophilic which means that moisture spreads readily over these surfaces. It is the source of abundant natural polymer after rice straw and rice husk. The material is less expensive, high mechanical strength, biodegradable and high water absorption but it releases water so fast. Since many of the developing countries growing coconuts are not utilizing coconut husk to produce value added products.

In Myanmar, the coconut husk is an agro-industrial by-product. Many tons of coconut husk are generated annually across Myanmar and these are treated as wastes. It also pollutes the nearby receiving water body by changing the physio-chemical properties. Sustainable management of coconut husk can be achieved by converting it into useful products through suitable techniques.

The coconut husk is composed of coir dust and fibre. The coir dust is about 70% of the weight of the coconut husk. The coir dust from the coconut husk can be extracted easily by soaking and beating [6]. By using coir dust, the utilization of water resources is improved and it is important factors for agricultural products. The main aim of the research work is to apply the peaceful use of nuclear techniques for improvement in agricultural productivity. The other objectives are to reduce the agricultural wastes by recycling them into useful products and to investigate the effect of gamma radiation on the synthesis of super-absorbent and their applications for crops. In this present work, Co-60 gamma radiation effects on the graft copolymerization of coir dust on acrylic acid monomer for the synthesis of super water absorption materials were studied. The parameters such as radiation dose and the amount of acrylic acid monomer in potassium hydroxide (KOH) were investigated in order to determine the optimum conditions for the grafting polymerization. The criteria are emphasized by the optimum conditions of important parameters to give a maximum amount of water absorption. The graft copolymer was characterized by FTIR and SEM [4].

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II. EXPERIMENTAL SECTION

A. Materials and Procedures

Materials

Coconut husks were collected from Yatanapon Market, Mandalay region. Acrylic acid (99% purity), Potassium hydroxide and ethanol (commercial grade) were used.

Extraction of Coir Dust from Coconut Husk

Coconut husks were soaked with water in the fibre tank for two weeks and then bete the husks. After that, separation of coir dust and fibre was carried out by manual. After separation and removing coir fibre, the coir dust remaining in the tank was filtrated and dried under sunlight. The dry sample was crushed with blander and sieved with 0.0232 inch wire sieve.

Graft Copolymerization of Coir Dust-Acrylic Acid Using Co-60 Gamma Radiation

Preparation of solution (1); Potassium hydroxide (30 g) KOH was mixed with 150 ml of deionised water and stirred at room temperature for 15 minutes. Preparation of solution (2); 30 ml of acrylic acid was added into the 70ml of deionised water and stirred for 15minutes.

After preparing each of solutions, solution (2) was dropped slowly into the solution (1) and stirred for 20 minutes to obtain potassium-acrylate solution. The coir dust sample 30g was dropped slowly into the prepared potassium-acrylate solution and stirred by glass rod until the solution and sample mixed thoroughly. Different concentrations of acrylic acid monomer (30%, 40%, and 50%) were used for the experiments.

Mixture samples were packed in polyethylene (PE) bags and stabilized for four hours and then irradiated on gamma Co-60 source in the dose range: 10, 15, 20, 25, and 30 kGy at dose rates of 1.4381kGy/hr. Irradiated Samples were cut and dried at 50°C with hot air oven and then the dried samples were soaked in ethanol for 24 hours to remove ungrafted monomer after that the polymer was soaked in hot water at 60°C for 12 hours. The swollen samples were filtered and dried at 50 °C until constant weight was obtained.

B. Analytical and Determination Methods

Scanning Electron Microscope (SEM)

Scanning electron microscope was used to investigate on the structural modifications of coir dust (CD) and grafted polymer.

Fourier Transformed Infrared Spectroscopy

Identification of functional group of the active components based on the peak values were achieved by Fourier transformation infrared (FTIR) analysis. The IR is divided into three regions; namely the near, mid and far IR. The mid-IR is the most common region to identification and study of organic compounds based on fundamental vibrations and associated rotational-vibrational structure. IR spectroscopy is a popular method for characterizing polymers^[13].

The FTIR spectra of the original coir dust and grafted coir dust acrylic acid were recorded by FTIR spectrophotometer

(Shimadzu, Japan) in the mid-infrared region. The FTIR spectra were recorded at wave numbers from 400-4000 cm⁻¹^[9].

Determination of Grafting

The grafting efficiency (GE) of coir dust-acrylic acid was determined as follows:

$$GE (\%) = (W_p - W_o) \times 100 / W_m$$

where W_o , W_p , and W_m are the determined weight of coir dust, purified polyacrylate grafted coir dust and acrylic acid monomer respectively^[14].

Swelling Measurement

A sample of the polymer (1.0 g) was dispersed into 250 ml of ordinary water and allowed to swell with mild agitation. The steady state or equilibrium swelling was determined by allowing overnight for absorption. The swollen samples were filtered and surface water was dried carefully. The quantitative figures of swelling degree were calculated as shown in equation.

$$q_t = \frac{q_{ss} - q_{ds}}{q_{ds}} \times 100\%$$

where q_t is swelling at time t, q_{ss} is weight of the swollen or water-absorbed polymer at time t and q_{ds} is weight of the original dry superabsorbent polymer respectively^[8].

III. RESULTS AND DISCUSSION

A. Investigations on Structural Modifications Coir Dust (CD) and Grafted Polymer

In order to get information about the morphology of coir dust SEM images were taken. The scanning electron microscopes of coir dust (CD) and grafted super absorbent are shown in Fig.1, and Fig .2.

From Fig.1, it is possible to see that coir dust sample has smoothening of surface and honeycomb like structure.

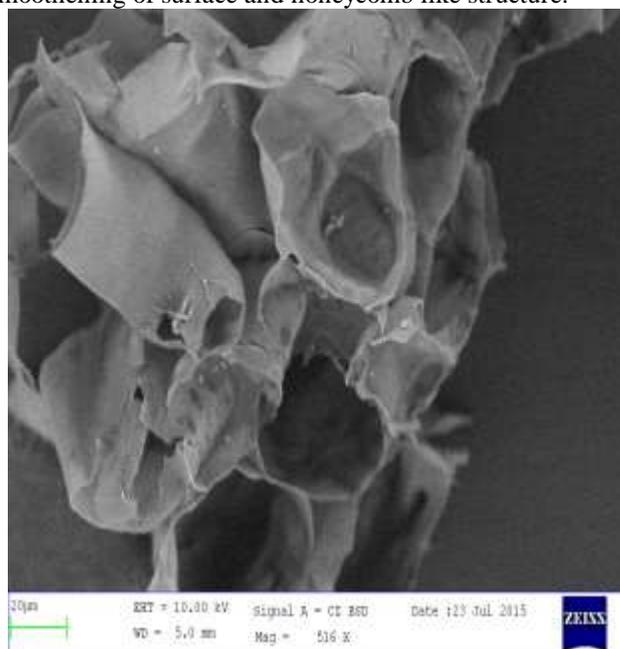


Fig.1. SEM image of original coir dust at 20µm

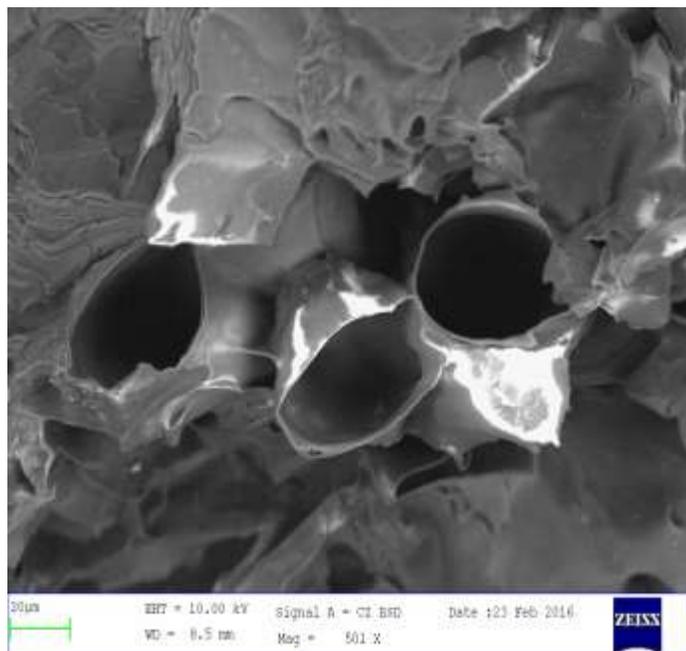


Fig.2. SEM image of grafted sample of 20kGy dose at 20µm

According to the Fig.2, it can be seen glutinous form after irradiation grafting of acrylic acid monomer on to the coir dust backbone. The SEM photo of grafted sample has course surface rather than smooth surface. These morphological changes were due to grafting of acrylic onto coir dust.

B. Characterization of Acrylic Acid, Coir Dust (CD) and Grafted Copolymers using FTIR Spectroscopy

The FTIR spectra of the acrylic acid, coir dust sample and grafted copolymer are shown in Fig.3, Fig.4, and Fig.5.

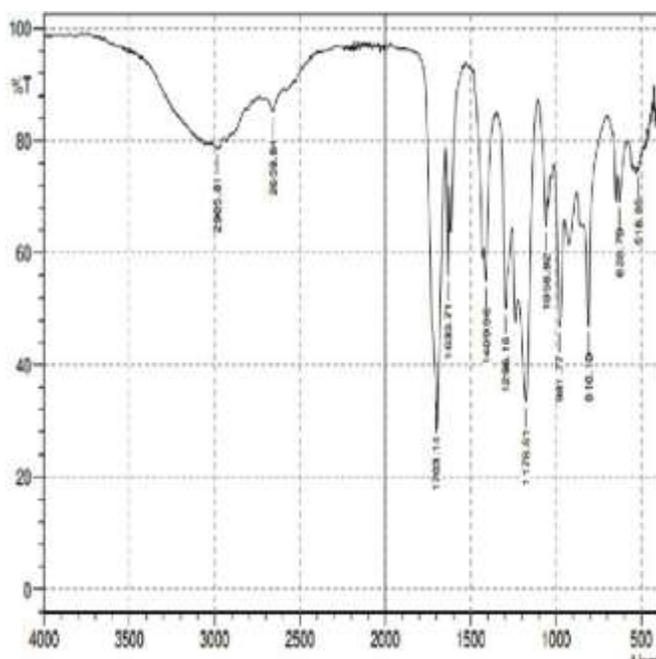


Fig.3. FTIR spectra of acrylic acid

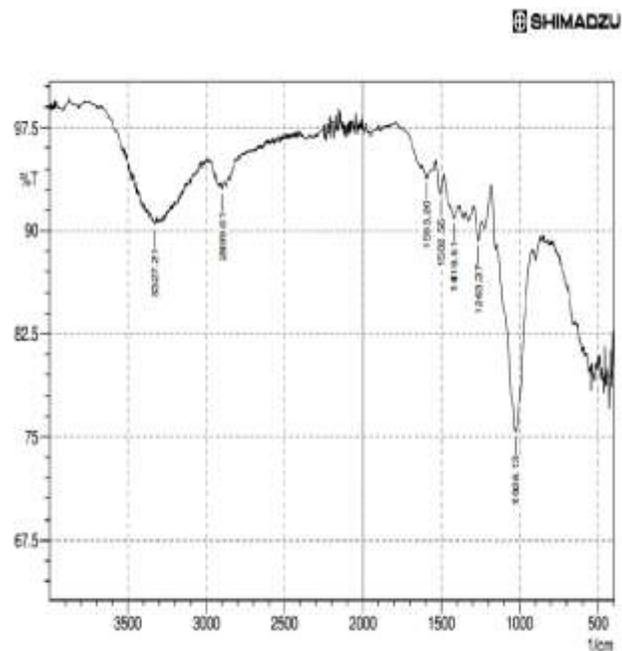


Fig.4. FTIR spectra of coir dust sample

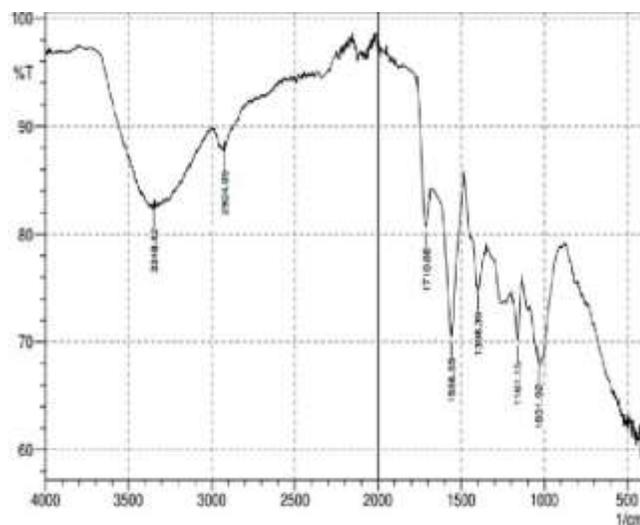


Fig.5. FTIR spectra of grafted sample obtained from treatment at 20kGy dose

In FTIR studies, the mid-infrared spectrum ($4000\text{-}400\text{cm}^{-1}$) can be approximately divided into four regions. They are X-H stretching region ($4000\text{-}2500\text{cm}^{-1}$), the triple-bond region ($2500\text{-}2000\text{cm}^{-1}$), the double-bond region ($2000\text{-}1500\text{cm}^{-1}$) and the fingerprint region ($1500\text{-}600\text{cm}^{-1}$).

Fundamental vibrations in the $4000\text{-}2500\text{cm}^{-1}$ region are due to O-H, C-H and N-H stretching. According to the results of FTIR spectroscopy, spectra of acrylic (Fig.3), coir dust (Fig.4), and grafted sample (Fig.5) showed nearly the same profile. However, the intensities of the absorption bands were different.

From Fig.5, it was observed that the appearances of the bands corresponding to the triple bonds (at 2303cm^{-1} and at 2105cm^{-1}) were appeared in the spectrum of grafted sample.

These changes provided strong evidence of the grafting of acrylic monomer onto coir dust.

The another obvious characteristic of the grafted sample indicated the appearances of absorption bands (at 1710.06 cm^{-1} and at 1556.55 cm^{-1}) which were not observed in the spectrum of original coir dust. These absorption peaks were due to

-COOH stretching vibrations and -CH₃ stretching. Taking into account the results obtained by the FTIR analysis it is possible to say that the grafting reaction was successful.

C. Determination of Grafting

TABLE 1. EFFECT OF RADIATION DOSES ON GRAFTING EFFICIENCY AT DIFFERENT RATIO OF MONOMER

| Radiation Doses (kGy) | Coir Dust (g) | Monomer concentration (30%) Grafting Efficiency (%) | Monomer concentration (40%) Grafting Efficiency (%) | Monomer concentration (50%) Grafting Efficiency (%) |
|-----------------------|---------------|---|---|---|
| 10 | 6 | 31.74 | 54.46 | 52.48 |
| 15 | 6 | 35.90 | 59.41 | 69.32 |
| 20 | 6 | 43.62 | 62.46 | 83.16 |
| 25 | 6 | 50.14 | 66.83 | 90.09 |
| 30 | 6 | 51.90 | 71.78 | 95.06 |

Table-1 showed the variation of grafting efficiency on different radiation doses. It is observed that radiation has a considerable effect on the grafting reaction. According to the results obtained the grafting yield increases with increase in radiation dose. It can be explained that the high radiation dose

can induce active grafting sites on the coir dust for the grafting of monomer. Similarly, the grafting efficiency also increases with the monomer increase.

Fig.6 showed the grafting yield increases clearly with increase in radiation doses.

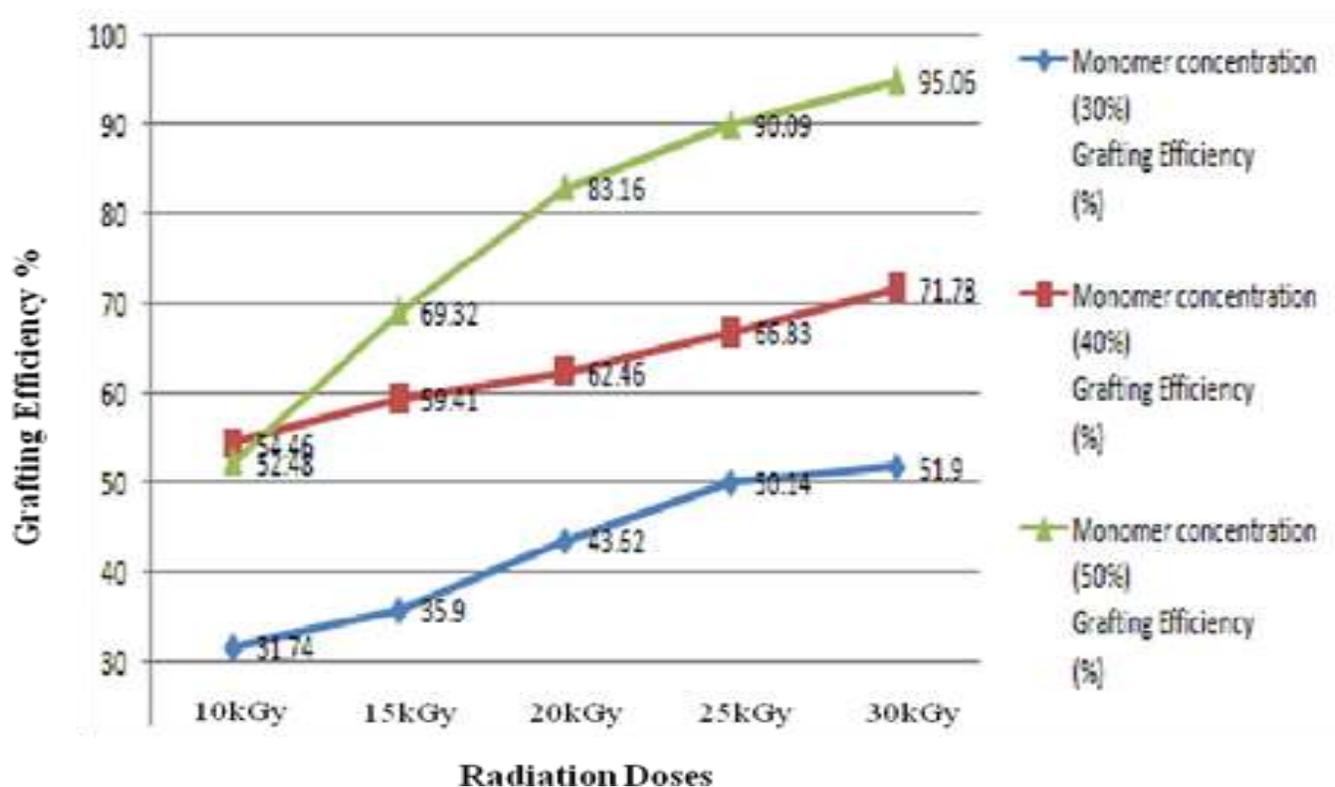


Fig.6. Grafting Efficiency (GE %) at Different Monomer Concentration

D. Effect of Radiation Dose on Swelling Degree

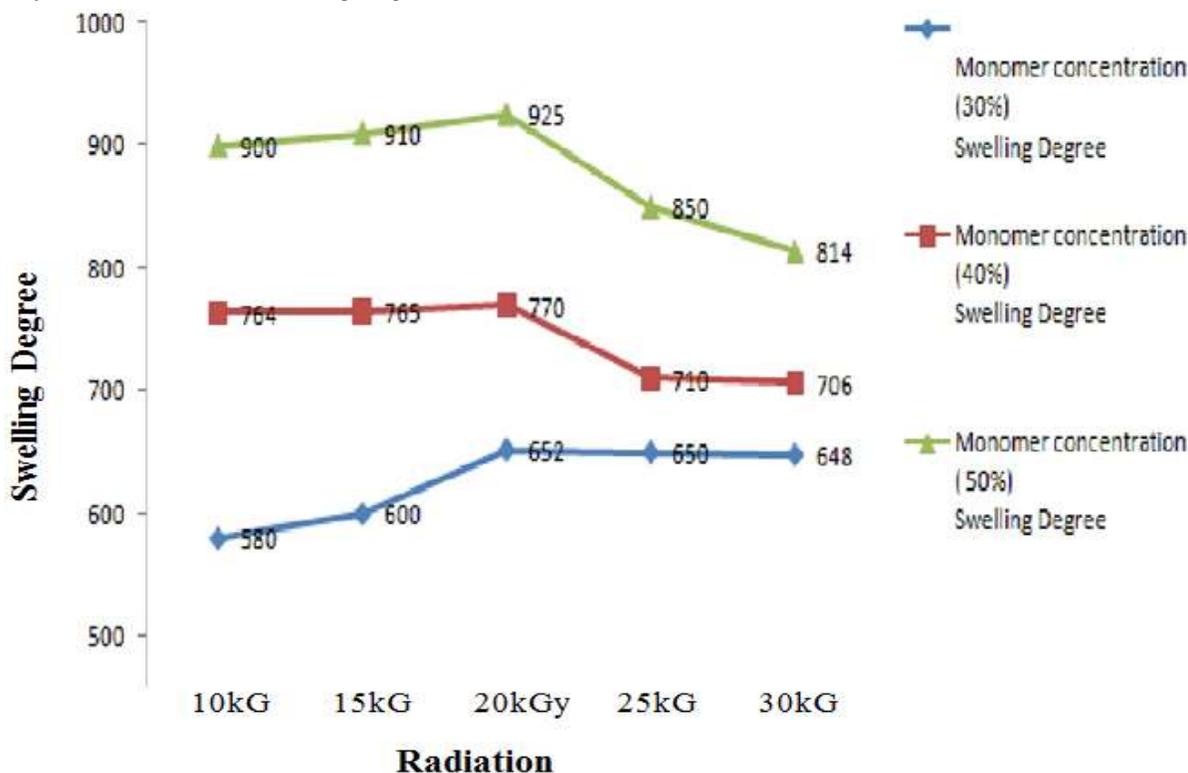


Fig.7. Swelling Degree at Different Monomer Concentration

By studying the results from the graph of swelling degree measurement, it was found that the swelling of super water absorbent increased with the increased radiation dose; the saturating value achieved at 20kGy and then decreasing in the high dose range. Because of, the extent of swelling represents a competition between two forces. As the polymer chains in the cross-linked polymer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The volumetric swelling reaches steady state when the two forces balance each other.

The effects of acrylic monomer concentration on the swelling degree of different doses of the absorbent polymers are shown in Fig.7. In Fig.7, swelling degree of all monomer concentration increased with increasing doses, and achieved saturating value at 20kGy and then decreasing in the high dose range. It is also seen that swelling degree of higher monomer concentration is greater than lower monomer concentration because at higher concentration of monomer, the free radicals come closer than lower concentration of monomer and that tends to form more cross-links in the coir dust.

IV. CONCLUSIONS

From studies and the obtained results, it may conclude that coir dust can be used as a material for preparing super water absorption polymers by grafting with sodium acrylate using radiation techniques.

SEM and FTIR spectra confirmed the grafting on acrylic acid onto coir dust. From the obtained grafting efficiency results, it was found that the higher the radiations dose the higher the grafting efficiency of super water absorbent. However, swelling degree was found decreasing in higher radiations dose.

The optimal parameters for preparation of super water absorbent are 20kGy irradiation doses, coir dust 6g, KOH of 20% and acrylic monomer concentration 50% respectively.

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REFERENCES

- [1] Nguyen Trong Hoanh Phong, Nguyen Tan Man, Nguyen Tuong Ly Lan, Tran Thi Thuy, Le Nan Toan, Le Huu Tu, Le Xuan Cuong, Pham Thi Sam, Le Hong En and Le Hai, Vietnam Atomic Energy Institute, "Preparation of Super Water Absorption Polymer By Radiation Grafting of Sodium Acrylate onto Coir Dust for Agriculture use", the annual report for 2012, VINATOM.
- [2] A.A.L. Goncalves, A.C.Fonseca, I.G.P.Fabela, J.F.J.Coelho, A.C.Serra, "Synthesis and characterization of high performance superabsorbent

- hydrogels using”, Department of Chemical Engineering, University of Coimbra, Rua Silvio Lima-Polo, 3030-209, Coimbra.
- [3] Masao TAMADA and Tamikazu KUME, environmental polymer Group,” Radiation Processing of Natural Polymer”, December, 2006.
- [4] Ray, Saha, Nur, Saha, Hoque and Saha,”Study on the preparation of polymer-grafted coir fibre, 48(4) 2013.
- [5] Hussein Omidian, Seyed-AliHashemi, Fahimeh Askari, Siavash Nafisi,”Swelling and Crosslink Density Measurements for Hydrogels,” Polymer Research Center of Iran, Tehran, I.R.Iran, January 1994.
- [6] Belas Ahmed Khan,” Uses of Coir Fiber, Its Product& Implementation of Geo-Coir in Bangladesh,” Daffodil International University Journal of Science and Technology, Volume 2, Issue 2, July 2007.
- [7] K.Rajjumar, Ranjith.P, Indian Rubber Manufacturers Research Association,” A value chin for Coconut Firer and it’s by product manufacture of diversified products of higher value and better marketability to enhance the economic returns for farmer”, Maharashtra, PIN 400604, 2008.
- [8] Dian Ciolacu, Florin Ciolacu and Valentin I. POPA,” Amorphous Cellulose Structure and Characterization,” Cellulose chemistry and technology, July 26, 2010.
- [9] Wenbo Wang and Aiqin Wang,” Preparation, Swelling and Water-retention Properties of Cross-linked Superabsorbent Hydorgels Based on Guar Gum,” center of Eco-material and Green Chemical, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, advanced materials research vol. 96, pp 177-182, 2010.
- [10] Deepak Pathania and Reena Sharma, Department of Chemistry, shoolini University of Biotechnology and Management Sciences, Solan 173212, Himachal Pradesh,” Synthesis And Characterization Of Graft Copolymers Of Methacrylic Acid Onto Gelatinized Potato Starch using Chromic Acid Initiator In Present Of Air,” February 2012.
- [11] Mizi Fan, Dasong Dai and, Biao Huang, Agricultural and Forestry University,” Fourier Transform Infrared Spectroscopy for Natural Fibres,”.
- [12] A.U.Israel, R.E.Ogali, O.Akaranta, and I.B.Obot, Department of Chemistry, University of Uyo, Uyo, Nigeria,” Extraction and Characterization of Coconut Coir Dust”, Dec, 2011.
- [13] Jose Luis Rivera-Armenta, Cynthia Gracieal Flores-Hernandez, Ruth Zurisadai Del Angel-aldana, Ana Maria Mendoza-martinez, Departamento de Metal- Mecanica, Mexico,” Evaluation of Graft Copolymerization of Acrylic Monomers onto Natural Polymers by Means Infrared Spectroscopy”



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